REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
25-11-2014	Final	22-April-2013 to 21-April-2014

4. TITLE AND SUBTITLE

Quantum Dot Superlattice Enabled Rational Design in Optoelectronics and Hydrogen Generation

5a. CONTRACT NUMBER
FA2386-13-1-4074

5b. GRANT NUMBER
Grant AOARD-134074

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)

Professor Leong Chuan Kwek

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Nanyang Technological University
50 Nanyang Avenue
Singapore 639798
Singapore

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AOARD
UNIT 45002
APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR/IOA(AOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-134074

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution A: Approved for public release. Distribution is unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

For the first time, the excitonic properties of realistic CdS and CdTe tetrahedral clusters have been investigated by first principle density functional theory method with quasi-particle corrections and many body electron-hole interactions. Specific aims of the research included characterization of the confinement effects on band gap and the exciton binding strength with an ultimate goal to address charge relaxation in optoelectronic devices. The computed optical transition energy is in excellent agreement with the measured value and salient features involving the quantum confinement effect are clearly revealed. This project provided deeper understanding of the microscopic picture of excitation, confinement, and associated charge relaxation relevant to optoelectronic devices.

15. SUBJECT TERMS

Quantum Dots, Optoelectronic Applications, Charge Transfer, Superlattices, Density Functional Theory, Coupling Strength, Coherent Transport

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Kenneth Caster, Ph.D.
U	U	U	SAR	5	**19b. TELEPHONE NUMBER** *(Include area code)* +81-42-511-2000

Final Report for AOARD Grant FA2386-13-1-4074 "Quantum Dot Superlattice Enabled Rational Design in Optoelectronics and Hydrogen Generation"

April 21, 2014

PI and Co-PI information: KWEK Leong Chuan; lckwek@ntu.edu.sg; Nanyang Technological University, 50 Nanyang Ave. Singapore 639798; Phone: +6590095232; Fax: +6567944941

Period of Performance: 04/22/2013 – 04/21/2014

Abstract:

For the first time, the excitonic properties of realistic CdS and CdTe tetrahedral clusters have been investigated by density functional theory method with quasi-particle corrections and the explicit coupling between electron and hole. The achieved understanding of microscopic picture of excitation, confinement, and associated charge relaxation will generate impacts on optoelectronic devices, and hydrogen generation under sunlight.

Introduction:

Intensive research works have been made on inorganic semiconductor nano size quantum dots (QDs) which exhibit tunable size dependent optoelectronic properties. QDs play important roles in optoelectronic technology owing to the high extinction coefficient and narrow emission spectra. Enabled by the remarkable enhancement in computing power, it is becoming feasible to study excitonic properties in realistic QDs. In this work, our specific aims include the characterization of the confinement effects on band gap and the exciton binding strength. The ultimate goal of the work is to address charge relaxation in optoelectronic devices, for instance, high speed photodetectors.

Experiment: Description of the experiment(s)/theory and equipment or analyses.

We investigated the exciton properties of the tetrahedral CdS and CdTe clusters through first principle density functional theory calculation (DFT) with with quasi-particle corrections and many body electron-hole, interactions. We first computed the ground state wavefunctions by the local density approximation based exchange-correlation functional using density functional theory. Normconserving pseudopotentials with a kinetic energy cutoff of 50 Ry are employed during the calculations. Each structure is fully relaxed until the force convergence reaches 0.01 eV/Å. The G_0W_0 approximation is used for the self-energy operator to make the quasiparticle corrections to the band gaps computed by local density functional approximation. The plasmon-pole approximation is introduced to treat the screening. The electron-hole interactions are computed by solving the Bethe-Salpeter equations.

Results and Discussion:

In this work, we focus on the capped tetrahedral CdS and CdTe clusters. The optimized Cd-S and Cd-Te bond lengths are 2.56 Å and 2.79 Å respectively, in a good agreement with the experimental values, i.e. 2.55 Å and 2.77 Å (ref. 1 and 2). We then computed the LDA band gap E_g^{LDA}, GW (G0W0) corrected band gap E_g^{GW}, the absorption (1st excitation) energy E_{abs}, and thebinding energy of exciton $E_b = E_g^{GW} - E_{abs}$. The absorption spectrum, exciton wavefunction, and HOMO/LUMO are presented in Fig. 1. The self-energy error in DFT is corrected by GW. The electron-hole shows strong binding feature. Clearly, the dominant component in the lowest excitation is from HOMO-LUMO transition. The HOMO of $Cd_{17}S_{32}H_{28}Na_2$ is four-fold degenerated, located at the four corners of the tetrahedral, while the LUMO is mainly distributed in the core and middle parts of the edges. The remarkable charge transfer character is reflected in the excitation from HOMO to LUMO.

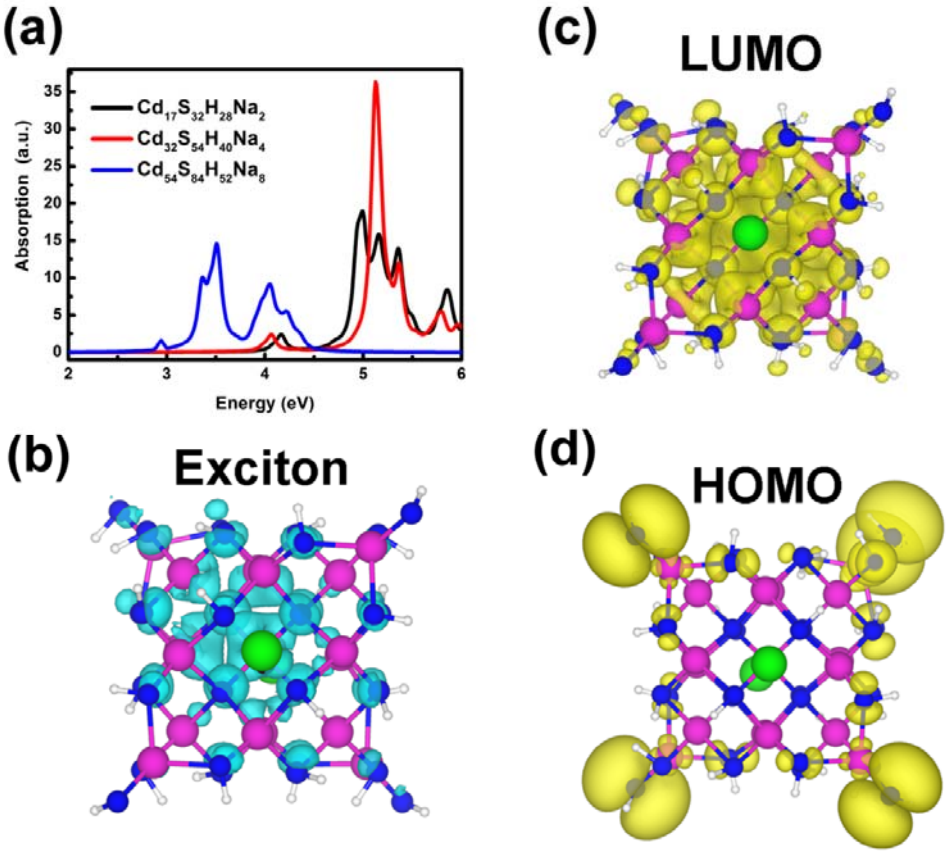

Figure 1. (a) Absorption spectrum for the three CdS clusters, (b) exciton wavefunction of the first exciton peak in the $Cd_{17}S_{32}H_{28}Na_2$ structure. (c) and (d) show LUMO and HOMO of the $Cd_{17}S_{32}H_{28}Na_2$ structure.

As shown in Table 1, the radius size for the three CdS clusters are 0.65 nm, 0.81 nm and 1.15 nm for the Cd_{17}, Cd_{32} and Cd_{54} clusters respectively, the R is defined as the root mean square of the longest and shortest lengths in the cluster. When the size of the cluster increases, the confinement effect decreases, the band gaps decrease from 5.7 eV to 4.1 eV. Note that the exciton binding energy is very large, around 1.0 eV, indicating a strong electron-hole coupling in the CdS clusters. Interestingly, the confinement is also reflected in the reduction of E_b from 1.5 eV to 0.9 eV with the size of the cluster increases. The same trend holds in CdTe clusters. The smaller electronegative value of Te, as compared with S, leads to the narrower band gap, lower absorption edge, and slightly weaker exciton binding strength. Since these clusters are quasi 0D structure, the exciton bevavior is different from the bulk materials. The size dependent exciton binding unravels the relatively stronger screening in CdS and CdTe clusters as compared with other low dimensional materials, i.e. carbon nanotubes, graphene nanoribbens, graphene oxide quantum dots.

Table 1: Radius of each cluster R, LDA band gap E_g^{LDA}, GW corrected band gap (E_g^{GW}), the first absorption energy (E_{abs}), and exciton binding energy (E_b) for the CdS clusters. R is in unit of nm and all the energies are in unit of eV.

Clusters	R	E_g^{LDA}	E_g^{GW}	E_{abs}	E_b
$Cd_{17}S_{32}H_{28}Na_2$	0.65	1.5	5.7	4.2	1.5
$Cd_{32}S_{54}H_{40}Na_4$	0.81	1.3	4.9	3.7	1.2
$Cd_{54}S_{84}H_{52}Na_8$	1.15	0.8	4.1	3.2	0.9
$Cd_{17}Te_{32}H_{28}Na_2$	0.72	1.3	5.3	3.8	1.4
$Cd_{32}Te_{54}H_{40}Na_4$	0.93	1.1	3.8	2.8	1.0
$Cd_{54}Te_{84}H_{52}Na_8$	1.28	0.6	2.9	2.4	0.8

In summary, the *ab initio* (with electron-hole coupling) results of exciton in CdS quantum dots are reported for the first time in this work. The computed optical transition energy is in excellent agreement with the measured value. The salient feature of quantum confinement effect is clearly revealed. The tunability by chemical alloying Te with S is demonstrated by the change in energy gaps. For the follow-up work, we would like to study optical properties in quantum dot superlattices which offer a novel promising platform for manipulating light matter interaction and charge separation. The important questions include how physical properties develop when regular macroscopic structures are built up by interactions between quantum dots? which is the

key fundamental processes in many strategically important optoelectronics applications.

References:

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2. Rogach, A. L.; Katsikas, L.; Kornowski, A.; Su, D. S.; Eychmuller, A.; Weller, H., Synthesis and characterization of thiol-stabilized CdTe nanocrystals. *Physical Chemistry Chemical Physics 1996, 100 (11), 1772-1778.*

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

One manuscript is currently being prepared, and to be submitted soon. The exchange of results obtained in this project with Dr. Ruth Pachter, and her team member, Kiet Nguyen at Air Force Research Laboratory.

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Important Note: If the work has been adequately described in refereed publications, submit an abstract as described above but cite important findings to your above List of Publications, and if possible, attach any reprint(s) as an appendix. If a full report needs to be written, then submission of a final report that is very similar to a full length journal article will be sufficient in most cases.